Results of Summer 2008 Water Quality Research Project in the Valparaiso Chain of Lakes Watershed

Submitted by

Lindsey Gilman
Windy Santa Cruz
Dr. Jonathan Schoer

Department of Chemistry
Valparaiso University
Valparaiso, IN 46383

April 15, 2009

Overview Of the Water Quality in the Valparaiso Chain of Lakes Watershed

With the completion of our fourth year of sampling in the chain of lakes we have established baseline values for many parameters that affect the water quality and are beginning to observe trends. In general, results for the less developed (smaller amount of residential and commercial/industrial uses) lakes are similar to those found in 2005-2007 testing, suggesting the WQ in these lakes has become stable. However, some parameters on the more developed lakes, are changing in ways that suggest some steps need to be taken to preserve the overall water quality. For example, conductivity in Canada, Deep, Long, Mink, Moss and Wauhob lakes remains at a level lower than that typically found in NW Indiana. On the other hand, Bullseye Lake at 1600 μS/cm (four times higher than the other watershed lakes) and Spectacle Lake both have conductivity levels higher than those typical of NW Indiana. Explanations for the differing levels are generally attributed to the size of the lake and surrounding land use. For example, Bullseye Lake is adjacent to the intersection of two major roadways and receives substantial run-off (including road salts, automotive debris, and sediment) from these roads. Identifying the specific source of the increased conductivity is a challenge, so a chloride probe was added in 2007. Future work with this and other ion-selective methods will hopefully lead some insist to the increasing levels in some lakes.

Dissolved oxygen levels in the lakes are also generally acceptable to elevated. The majority of the lakes generally remained in the 6-9 mg/L of dissolved oxygen range (values above ~5 mg/L are generally viewed as acceptable); thus, there was little concern for most lakes. However, in seveal case the DO was actually too high, suggesting hyperactive plant activity and setting the stage for a possible future fish kill when the plants die. For example, higher levels are now being observed at 10 to 14 mg/L for Mink and Canada Lakes.

Nutrient levels (phosphates, nitrates and nitrites) throughout the watershed continue to be of concern, especially phosphorous. In some case, the phosphorous to nitrogen ratio was found to be inverted from that normally found in aquatic systems (~16 N:1 P), so excessive plant growth is expected, thus reducing water clarity and temporarily raising dissolved oxygen levels. High nutrient levels also contribute to elevated conductivity levels.

INTRODUCTION

The land comprising the Valparaiso Chain of Lakes watershed has been molded by both its ancient geologic history and by more recent modifications by humans. After the last ice age, the retreating glaciers left behind portions of calved ice that created large depressions, known as kettle lakes, and rounded hills called knobs. The Valparaiso Chain of Lakes is part of this knob and kettle topography that dots Northwest Indiana. Before the arrival of white settlers in the region, the vibrant culture of the Pottawatomie dominated the area. In general, they made only minor modifications to the landscape. However, as western settlers began moving west, Northwest Indiana developed into a major trading post, an agriculturally productive region, and a desirable vacation spot. These activities brought major changes to the land use in the region. Its popularity brought resorts and summer homes to the Flint and Long Lakes. In an effort to increase accessibility to the surrounding cities, the interurban railroad line pushed its way through the forests and shorelines. Continued growth and development lead to the town that now occupies much of the watershed. Even as the area continues to develop the importance of protecting the Valparaiso Chain of Lakes watershed's rich history, uniquely preserved topography, and water quality is recognized by people in the community, the VLACD, and the Valparaiso University Chemistry Department.

During the summer of 2008, Dr. Jonathan Schoer, Lindsey Gilman, and Windy Santa Cruz of the Valparaiso University Department of Chemistry continued the monitoring of the water quality of the local watershed's major lakes and streams. In the past, 30 years various groups and organizations have collected data on specific lakes watershed, but few reports compare parameters involving all the major lakes during the same time period. This project is unique in that it involves regular testing throughout the entire Valparaiso Chain of Lakes Watershed. J.F. New recently prepared a report for the Lake Area Conservancy District in 2001 that adds to the Indiana State Board of Health 1970's report. It is with these two reports in mind that Valparaiso University students under the leadership of Dr. Jonathan Schoer began the Valparaiso Chain of Lakes Watershed Water Quality Project.

The testing completed in the summer of 2008 focused on basic chemical and physical parameters that are frequently used as indicators of water quality. These include temperature, pH, dissolved oxygen, nutrients, clarity, and conductivity. Additional tests recently added include NH_4^+ (added summer 2008) and depth profiling (added summer 2007). Other parameters measured in past years, but not tracked in 2008, are total solids, E. coli and fecal coliforms, and heavy metal analysis. Heavy metals (zinc, cadmium, iron, lead and copper) were measured in the summer of 2007, but were generally found to be present at negligible levels, which is consistent with the pH of lakes (typically greater than 7 which will largely precipitate these ions as hydroxides). During the summer of 2008 new or revised methods for the analysis of nitrates, dissolved reactive phosphorus, and total phosphorus were initiated. However, technical issues prevented us from completing analyses with the new methods. These methods will be revisited in 2009 and it is anticipated that the new methods will be used regularly thereafter.

During the summer season, samples were collected on a rotating basis in which each lake was tested two times. Because this was the fourth year collecting data, a good baseline has now been established for the parameters in many of the lakes including how some parameter may fluctuate depending on sampling date and conditions. Because parameters fluctuate for a variety of reasons, long-term trends are more valuable and we are now in a position to start tracking changes. Our long-term plan is to include testing the lakes and streams quarterly during the academic year and implementing new QA and QC methods to improve the reliability of our results.

MATERIALS AND METHODS

Our sampling techniques and measurements were in accordance with procedures provided by instrument manufacturers, including CHEMetrics, Vernier, Industrial Test Systems, and Micrology Laboratories, YSI, and Hach. The parameters we focused on this year were temperature, pH, conductivity, phosphate and nitrate levels, dissolved oxygen, water clarity, and heavy metals. Due to instrument difficulties not all parameters were completed at all points in time. Instruments were calibrated daily in the laboratory and were often calibrated in the field. Here is a brief description and list of all the instruments that were used.

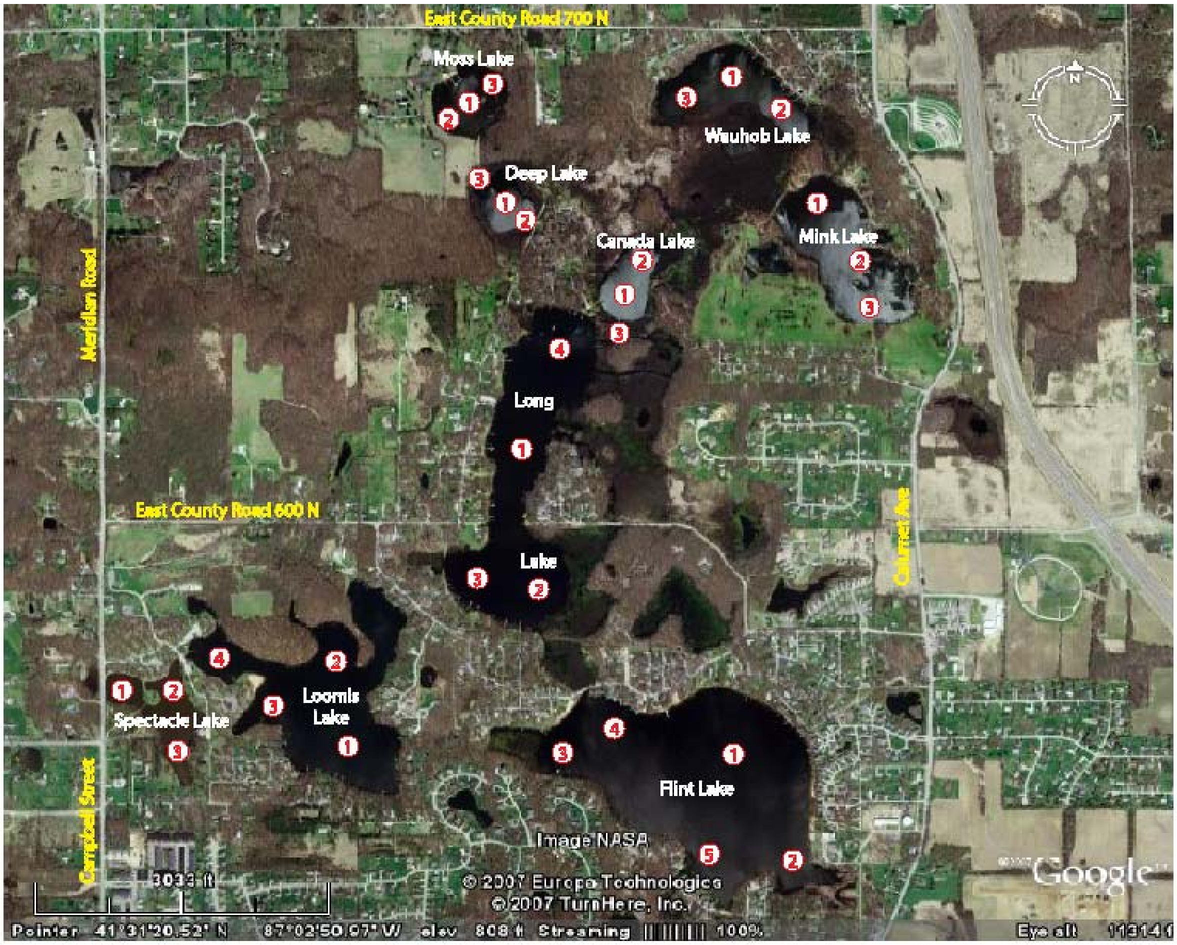
1. Vernier Lab Pro – This device is an interface that allows for students to use a Texas Instrument calculator and various probes to test different parameters.
2. TI-83+ or TI89 – Both of these calculators were used in conjunction with the Lab Pro interface via the Datamate Program.

3. Vernier pH probe – Used with the Vernier system to assess the acidity or alkalinity of the target environment. The sensor was partially submerged in water until the reading stabilized.
4. Vernier Dissolved Oxygen Probe – Used with the Vernier system to measure the amount of dissolved oxygen in the water (mg/L). The sensor was partially submerged in water until the reading stabilized.
5. Vernier Conductivity Probe – Used with the Vernier System to assess the overall ion concentration of the water in a desired area (micro S/cm). The sensor was partially submerged in water until the reading stabilized.
6. Vernier Turbidity Sensor – Used with the Vernier System to measure the clarity of a sample of water from the environment. This test was done on site by filling a small capsule with water and then placing the capsule into the instrument.
7. Vernier Nitrate Probe – Probe also used with Vernier System. Probe measures the nitrate ion concentration in the water in ppm (mg/L). Tip of the probe was submerged into the water and once stabilized the reading was taken.
8. Vernier Chloride Probe - Used with the Vernier System, this probes measures the chloride ion concentration in the water by submerging the tip of the probe into the water and waiting for it to stabilize.
9. Vernier Ammonium Probe - This probe in conjunction with the Vernier System, measured the ammonium ion concentration. The tip of the probe in placed into the water and reading taken after the probe stabilized.
10. Garmin GPS Unit – The GPS unit was used to locate the sample sites within a couple yards. Reproducibility of test site location is crucial for developing trends.
11. Hydrolab depth probe - This probe is lowered directly into the water and measures the dissolved oxygen levels and temperature. Readings are taken at the surface and each foot until reaching the bottom.
12. Secchi Disk—This disk was used in conjunction with surveyor's tape to measure the clarity of the water. The disk placed into the water and lowered until it can longer be seen. The depth reading is taken (in meters). The probe was lowered even farther and then raised again until visible where another reading was taken. An average of the two depths was taken to give an approximate idea to where the visibility ends.

13. Detailed Lab Procedures for (DRP: Dissolved Reactive Phosphorus) and (DTP: Dissolved Total Phosphorus) are attached to the report.
14. Heavy Metal Lab Procedure: Used AA (Atomic Absorption) and standards to determine the absorbance of the samples. Then through Beer's Law ($A = \varepsilon BC$), the concentration was determined.

General Comments Regarding the Data and Results

The raw data and graphical representations of the past four summers of data collection are organized in an Excel spreadsheet that is attached as an electronic supplement. The data is sorted by lake, test site, parameter, and the date on which it was recorded. The number of sites varies between lakes depending on the number of major inflows and outflows of each lake, as well the overall size of the lake. The global positioning coordinates for each site can be found at the top of each table. Also included is a map with the sites numbered for convenience. The data is discontinuous for certain parameters due to occasional technical difficulties with equipment. These discrepancies are noted in the tables. For parameters measured both in the lab and in the field, only the lab value is recorded in the spreadsheet. Most of the sites had negligible concentrations of heavy metals in 2007, so only the significant values are contained in the attached Excel spreadsheet. No heavy metal analysis was completed in 2007.



Map showing the sampling sites for each lake in the Valparaiso Chain of Lakes watershed.

DISCUSSION

Clarity

Outstanding water clarity is generally denoted by a Secchi disk reading of 15 feet or more while poor water clarity is correlated with a reading of less than 5 feet (ISBH, 1975; Carlson, 1977—J.F. New). Water clarity, while useful for some applications, must be analyzed with additional parameters because it does not always reflect the general health of a body of water. For example, because of their greater productivity (plant and animal growth) streams and lakes in northwest Indiana have historically lower clarity values than do the lakes and streams in northern Wisconsin or Minnesota.

Water clarity can also be used in the classification of lakes. The trophic status of a lake can be estimated by Secchi disk readings. An oligotrophic lake has a reading of 16+ feet, a mesotrophic lake ranges from 6.5 to 16 feet, and a eutrophic lake bears a reading below 6.5 feet (Michigan Lakes and Streams Association 1993). Table 01 classifies each lake in the watershed based upon their average depth data.

Table 01. Classification of the lakes in the Valparaiso Chain of Lakes watershed.

	Classification
Bullseye	Eutrophic
Canada	Mesotrophic
Deep	Eutrophic
Flint	Mesotrophic
Long	Mesotrophic
Loomis	Eutrophic-Mesotrophic* (2007)
Mink	Eutrophic
Moss	Eutrophic-Mesotrophic
Round	Mesotrophic
Silver	Eutrophic
Spectacle	Eutrophic
Wauhob	Mesotrophic

The most accurate reading for lake classification is provided by the measurement obtained near the center of the lake. These are the readings that were used to compile Table 01.

However, testing sites along the shoreline were also monitored in an attempt to determine the effects of the variety of land uses along the edges of the water. Factors that influence water clarity readings include nutrient levels, algae blooms, soil erosion, zooplankton that feed on algae, and the amount of activity in the water. (Michigan Lakes and Streams Association 1993).

Water clarity can provide useful information about the environment being tested. The depth of the clarity is related to the aquatic life present in the watershed, due to the aquatic plants need for sunlight to perform photosynthesis. In murky waters, light penetration is restricted from reaching the lake bed, which in turn limits the plants' production of vital oxygen for the aquatic ecosystem. The lack of sunlight penetration causes a decrease in dissolved oxygen levels at lower depths. Also as a result, the plants tend to grow near the surface of the water which can lead to a bloom of aquatic plants. Large quantities of sediment in the water absorb much of the sunlight, warming the water and causing greater dissolved oxygen depletion. The measure of the amount of sediment present in the water is defined as turbidity. If turbidity is too low, the water may be too clear, allowing for rooted aquatic plants to appear in the watershed. The low values for turbidity can be due to a decreased plankton population in the watershed.

Water clarity throughout the chain of lakes is on average within an acceptable range. For Northwest Indiana, the lakes heavily utilized by the public tend to have acceptable clarity values. In the Valparaiso Chain of Lakes Watershed, the clarity of the lakes decreased as the summer progressed, as additional plant and zooplankton growth occurred. Silver and Bullseye Lakes experienced the most significant increase in plant cover during the summer. Loomis Lake experienced the most significant decrease in clarity in 2007, but these values returned to previous values in 2008.

Conductivity

In the Chain of Lakes, conductivity values are generally in an acceptable range for most species of fish endemic to this region, however there is significant variation between the lakes. The less developed lakes have conductivity values well below the average for Indiana, while lakes close to human activity have higher values. Most of the ions naturally found in the water come from contact with the soils. Due to the soil composition in NW Indiana, an average stream or lake has a typical conductivity between 400-500 μS/cm; a value low enough to support most fish and other aquatic species. The lakes in the watershed are generally below this range with the exception of Bullseye Lake, which has an average value of 1600 μS/cm. Spectacle Lake has also historically had conductivity values slightly higher than average for NW Indiana. This year was no exception with values generally at or above 600 uS/cm.

The high conductivity for Bullseye Lake is most likely a direct result of its small volume and the environment surrounding it. Factors that affect conductivity include a variety of pollution types; including run-off from vehicles, construction, road salting and other non-point sources (Water on the Web 1991). Canada, Deep, Long, Mink, Moss and Wauhob all have conductivity levels ranging from 100-300 μS/cm. The land use surrounding these lakes is generally much lower density residential, and during the study, use of these lakes and the surrounding land has remained largely unchanged. Therefore, the runoff associated with road salts, fertilizers, construction, and other sources of contaminants has had little impact on conductivity. Geographically, it is important to note that all six of the lakes with lower conductivity values are located along the northern fringes of the watershed, and the conductivity increases as the water flows further south.

The second grouping of lakes include those that are more affected by human activity, mainly through residential housing and light commercial activity. These lakes include Spectacle, Flint, Loomis, and Silver. In the past, Spectacle Lake experienced a large conductivity, reaching 1000 μS/cm in 2006. This value now appears to have stabilized at ~600 μS/cm. The likely causes of the increase are the lake's position adjacent to a more trafficked roadway (caused by multiple new residential developments) and the lake's small volume. The influx of road salts, fertilizers, and other runoff may also have greatly increased the conductivity over the past six years.

Flint and Loomis Lakes have experienced slight increases in conductivity over the past six years, and like Spectacle, appear to be leveling off. The only outlet from the watershed is through Flint Lake so it is affected by the other lakes as the water flows southeast. Therefore, Flint often reflects the changes seen in the other lakes. Loomis Lake receives water from Spectacle Lake, so its conductivity is anticipated to follow Spectacle's trend. Also, due to the relative large volume of Flint and Loomis Lakes, the conductivity values are not changing as dramatically as the smaller lakes in the watershed.

Silver Lake, the shallowest lake in the watershed (maximum depth of ~4 feet) with significant macrophyte growth, behaves much like a wetland. Conductivity is steadily increasing in Silver Lake. This may be aggravated by the recent construction of a roadway through the wetlands area along the south shore of the lake, however additional monitoring will be needed to verify this trend.

It will be important to continue monitoring these four lakes, because changes in conductivity can be related to an influx of pollutants including sediment entering the water. An additional factor known to contribute to conductivity is the impact of wastewater pollution from failing septic tanks and fields. Due to the fact that many of lakes are surrounded by housing using septic systems and the probable increasing failure rate of these aging systems it is anticipated that conductivity will continue to rise unless the septic fields are repaired or replaced.

In 2007, a selective ion probe for chlorides was added to better identify the cause of the increase in conductivity. High conductivity values located near roads that receive direct runoff were expected to also have high chloride concentrations. In most lakes, this correlation was seen, but the chloride ion concentration increase was not sufficient to account for the entire increase in conductivity. Further study is required to identify other ions that may be active contributors. In the summer of 2008, the specific ion probe for ammonium was added. However, the values collected for the ammonium ion were extremely low, so additional specific ion probes are needed for additional testing on the sources of high conductivity. Alternatively an ion chromatography system could be used to identify the ions and there concentrations. Currently, the chloride ion concentration is not to exceed 230 mg/L according to the State of Indiana, however no samples exceeded this level.

Dissolved Oxygen (DO)

Dissolved oxygen measurements provide a method to monitor oxygen available for fish and other aquatic life. In general, healthy ranges for DO are between 5-9 ppm (or mg/L). Higher levels of dissolved oxygen typically indicate a large amount of algae (or plant) activity both above (i.e. lily pads, spatterdock, algae) and below the water's surface ("seaweed"). Also, weather can play a large role in DO levels. Sunny days mean more photosynthesis and thus higher DO levels. Excessive nutrients in the water also leads to more plant growth which again increases the DO. However, healthy ranges of DO depend on the type of aquatic life within that water system. Large fish usually need higher levels of DO while smaller can survive on less. For most lakes in the watershed, the DO levels ranged between 6-9 mg/L. Most fish can survive in waters with DO levels of 5 mg/L and above, but below this certain species start to reach the threshold of survival especially if the concentration is sustained over time.

For the past three years, Mink Lake has been of concern because of very low levels of DO, usually 2-3 ppm (suggesting active bacterial decay of previous plant gorwth). However, this year Mink lake showed the opposite behavior. DO ranged from 10 to 14 mg/L, well above the saturation level for the water. This is a clear indication of vigorous plant growth as was reflected in excessive growth of aquatic vegetation observed this summer.

Bullseye Lake also saw a jump in DO two years ago. During the summer of 2008, however, the levels were consistent with last year's of 7 mg/L. Changes such as these are very important to monitor, as well as the amount of aquatic plant. Both Mink Lake and Bullseye Lake appear staged for a major algae bloom and the subsequent fish kill when the algae dies and bacterial action begins.

Spectacle Lake also experienced a huge increase in DO this summer. The DO levels rose 3-7 mg/L on the lake depending on the sight. Other lakes seem to oscillate between high and low levels of DO. Both Silver and Loomis Lakes' level depend greatly on the amount of plant growth. Canada Lake which had been slowly decreasing in DO levels from 7 to 5 mg/L actually rose to 8-10 mg/L. None of the more widely used lakes (Flint, Long, Wauhob, Moss) experienced drastic changes in DO or exceptionally low DO values.

Depth Profiling

A depth profile was charted for each lake at its deepest point. Using these charts, the trends of DO and temperature vs. depth can be easily observed. In each lake, except Moss Lake, both water temperature and DO decreased as the depth increased as anticipated. In Moss Lake temperature decreased as expected; however, DO levels decreased steadily until a depth of 4-5 meters (depending on the site) and then abruptly increased to the values similar to that found at the surface and then decreases as expected. The existence of thermoclines in striated water is well known, however, the observed behavior is unexpected. We do not have an explanation for this phenomenon at this time.

Nutrients (generally considered to be phosphates, nitrates, and nitrites)

Nitrate levels in all lakes were below limits generally accepted for drinking water, 10.0 mg/L (EPA 2003), for all of the lakes. In general, levels fluctuated between 0 and 2 mg/L throughout the summer, but gradually increased. Long and Canada Lakes both had higher nitrate concentrations in 2006 and 2007 (~ 4 mg/L) than in 2008 when the value was ~0.2 mg/L. The nitrate concentration in Loomis Lake increased to 0.7 mg/L. However, much higher values were measured in Silver, Bullseye and Spectacle Lakes. (These three lakes also had the increase in DO levels.)

The nitrate level in Silver Lake increased to ~4 mg/L in June 2007 during construction of the Vale Park Road extension, which suggests nitrogen levels were impacted by runoff from Vale Park Road. The level decreased to ~1 mg/L in 2008, which was close to its value before the construction of the road. This value is still much higher than the most of the other lakes in the watershed for 2008. Ongoing monitoring is needed to see if the trend continues.

Spectacle Lake also had ~1 mg/L nitrate level and Bullseye Lake generally had ~2-3 mg/L throughout the summer. IDEM has identified the most probable sources for nitrates in Indiana as being commercial fertilizer, concentrated animal feed, and septic tanks. Since there is little agriculture in the watershed and most of the lakes have homes with septic tanks adjacent to them, the most likely source of the nitrates are fertilizer applied to yards by home owners, improperly functioning septic tanks, and run-off from roadways.

Although the nitrate levels are not extraordinarily high, the phosphorous levels in the lakes continue to remain detectable throughout the summer at almost every test site (at least 0.1 mg/L). This is the same situation that was observed in 2005, 2006 and 2007. When taken together with the nitrogen levels, the concentration of phosphorous implies that N is the limiting nutrient in the watershed. This pattern is atypical to the usual ratio of nitrogen levels to phosphorous levels (16N:1P). Phosphate is historically the limiting nutrient in an aqueous environment and this has been documented to be the historical norm for Valparaiso's Lakes as well (J.F. New). The observed inversion of this ratio indicates that plant growth in lakes could increase dramatically if there is an influx of nitrogen into the water. This observation is consistent with the observations of many homeowners across the watershed that there is increasing algae blooms in the lakes and that they are occurring far earlier in the year than in the past. The continued presence of higher than normal phosphorus concentrations implies that it would be wise to look at ways to decrease the inflow of nutrients into the watershed.

pH

As in previous years, the pH in the watershed was generally between 6.5 and 8.5. This range is typical for lakes in Indiana. In general, the pH was relatively stable for the majority of the lakes during the summer and was comparable to past years. In general, the lakes at the "top of the watershed (Moss, Wauhob, Deep) tended to have pH values closer to 7.0, while those further down the chain and those that are generally more heavily used had somewhat higher pH values. Loomis Lake had the highest pH this summer with a value of ~8.5 and has shown a steady a gradual increase in pH. Although this parameter plays a vital role in regulating the solubility of potentially toxic elements (such as aluminum), the current pH range for the lakes does not suggest any specific hazard from these currently exist. However, a change of one pH unit can have a drastic impact on water quality and could potnetially endanger the aquatic life if a decrease begins to occur (Kentucky Water Watch 1996).

Temperature

As expected, the surface temperature of the lakes increasd as the air temperature increasd. As observed in 2008, all of the lakes showed an increase in temperature as summer progressed. Temperature ranges were generally consistent with the values recorded in 2007. Surface water temperature also depends greatly on plant life. For example, spatterdock, a large leafy plant, shields the underlying water from the sun and helps to cool the water. However, algae (and sediment) traps the heat and increases the surface temperature. Consequently, lakes with lots of algae and submerged aquatic vegetation, such as Spectacle and Silver Lakes, had higher water temperatures. Other parameters are also affected by the water temperature. For example, cooler water can contain a greater amount of DO. Efforts should continue to be made to limit aquatic plant growth and reduce sediment influxes into the lakes.

HEAVY METALS

The presence of heavy metals in the lakes in the watershed is typical low (2007 results) and not an immediate concern. Thus, heavy metal testing of the water will only be performed every 2-3 years unless a change is noted. No heavy metal testing was conducted in 2008.

BUOY AND SONDE

In 2007, a buoy with a sonde capable of monitoring 7 water quality parameters and a telemetry system capable of acquiring constant data was purchased and installed in the far SE corner of Flint Lake. The sonde records 7 parameters recorded include chlorophyll, turbidity, dissolved oxygen, water temperature, pH, conductivity and depth. Readings were taken every 15 minutes and downloaded to a computer in the water treatment facility. In July of 2007, the buoy and sonde were installed and data was collected through early August. The buoy and sonde were again utilized to collect data from early April until November in 2008. The data is still be analyzed and correlated with weather events.

FUTURE PLANS (for this summer and beyond)

New to this project, data was collected during the fall of 2007. Hopefully, more researchers will be able to collect data not only in the summer, but also throughout the academic year. This will hopefully start a trend toward collecting quarterly data in conjunction with the summer work. Also, classes in GIS (geographical information systems) were taken by the students at the Pierce Cedar Creek Institute in July. Using a computer program, future researchers will be able to use GPS information to map the watershed and create maps specific to the research. Testing of heavy metals will continue at periodic intervals and pesticides for lower concentrations and better accuracy. A grant to purchase an ion chromatography system that can be used to identify specific ions will be submitted this summer. This will help identify the specific ions responsible for the high conductivity levels observed in some lakes. An additional grant is being written to upgrade to more rugged and reliable field instrumentation.

This summer students will work to increase the reliability and reproducibility of the phosphorous procedure. Increased QA and QC will also be established. Attached are the lab procedures developed for phosphorus. We are still identifying a higher accuracy nitrate method than the use of a nitrate-selective electrode. This will hopefully be finalized this summer. Continued involvement of the project in the community and region continues. We will be working with Shorewood Forest on Lake Louise this summer, with Save the Dunes Foundation in the Salt Creek watershed, and with the IDNL in the Great Marsh this summer. Continued research in international connections in Hangzhou, China are another important opportunity for future students. Entering into the fifth consecutive year of analysis, there is a pressing need to not only monitor the overall water quality of the area, but to also act on improving problem lakes.

Revised Method # 352.1 Approved for NPDES (Issued 1978)

Title: **Phosphorus, Dissolved Reactive Phosphate and Total Dissolved Phosphorus** (Colorimetric, Ascorbic Acid, Two Reagent)

Instrumentation: Spectrophotometer

Applicable Range of concentrations: = 0.01-1.2 mg/L

Summary of Method: Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to for an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration. **Ascorbic Acid solution is only good for 2 weeks, thus a fresh solution must be made for each analysis.**

Analysis should be made as soon as possible and if samples are to be preserved for longer than 24 hours, (2-mL) of conc. H_2SO_4 should be added per liter of sample and refrigerated.

Apparatus:

- Spectophotometer suitable for measurements at 880 nm with a light path of 1 cm
- Acid-washed glassware **must** be used for the analysis of phosphorus

Reagents Needed:

- **Ammonium molybdate-antimony potassium tartrate solution:** Dissolve 8 g of ammonium molybdate and 0.2 g antimony potassium tartrate in 800-mL of distilled water and dilute to 1-L
- **Ascorbic Acid Solution:** dissolve 15 g of ascorbic acid in 200-mL of distilled water and dilute to 250-mL. Then add 2-mL of acetone. ***This solution is stable for two (2) weeks.***
- **Sulfuric Acid (11 M):** slowly add 310-mL of conc. H_2SO_4 to approximately 600-mL of distilled water. Cool and dilute to 1-L.
- **Potassium Persulfate**
- **Stock Phosphorus Solution (100 ppm):** Dissolve 0.4393 g of KH_2PO_4 in distilled water and dilute to 1-L in a volumetric flask.
- **Standard Phosphorus Solution (5 ppm):** dilute 5.0-mL of stock solution using a Pipetman to 100-mL in a volumetric flask.

Dissolved Reactive Phosphorus (DRP) Procedure:

1. Pipette 25-mL of filtered sample into 50-mL graduated tubes (washed in an acid bath one day prior).
2. Add 1-mL 11 M Sulfuric Acid to each sample using a Pipetman
3. Add 4-mL of ammonium molybdate-antimony potassium tartrate solution using a Pipetman
4. Add 2-mL of ascorbic acid
5. Dilute to 50-mL

6. Prepare standards in the same fashion but add all reagents to the volumetric flasks and then dilute to a final volume of 50-mL (standard conc. = 0.0 (blank), 0.1, 0.2, 0.3, 0.4, 0.5 ppm)
7. Wait at least 5 minutes before analyzing at 880 nm on the spectrophotometer
    a. **The color is only accurate for an hour**

Dissolved Total Phosphorus (DTP) Procedure:

1. Pipette 25-mL of filtered sample into 50-mL graduated tubes (acid bathed one day prior)
2. Add 1-mL of 11 M Sulfuric Acid to each sample
3. Add 0.4 g potassium sulfate to each sample and mix
4. Add ~10-mL of EZPure water
5. Prepare standards in the same fashion but add all reagents to the 50-mL volumetric flask and then add ~10-mL of DDI water
6. Quantitatively transfer all samples and standards directly into in microwave tubes.
7. Microwave with an exposure of 30 minutes at 250^{o} F (121^{o} C) (P5 setting) - use program 'Water Research'
8. Allow samples to cool in a ice bath
9. Quantitatively transfer samples into graduated tubes (volumetric flasks for standards) sparingly using DDI
    a. **If any samples have evaporated off significantly, they will not be accurate and will need to be done again**
10. Add 2-mL of ascorbic acid using a Pipetman
11. Dilute samples and standards to 50-mL mark
12. Wait at least 5 minutes before analyzing at 880 nm on the spectrophotometer
    a. **the color is only accurate for an hour**

Literature Cited

1. Kentucky Water Watch, Limiting pH Values, www.state.ky.us/nrepc/water/wcpph.htm, April 1996.
2. Indiana Department of Environmental Management, Integrated Water Quality Monitoring and Assessment Report, 2004.
3. J.F. New, Valparaiso Chain of Lakes Diagnostic Study, 2003.
4. Ruth Francis-Floyd, University of Florida. Dissolved Oxygen for Fish Production. edis.ifas.ufl.edu/BODY_FA002. 2003
5. Michigan Lake and Stream Associations. The Secchi Disk—What is it? www.mlswa.org/secchi.htm 1993.
6. EPA, *E. coli* 0157:H7 in drinking water -- US EPA, www.epa.gov/safewater/ecoli.html,\ February 2005.
7. Water on the Web, Electrical Conductivity, http://waterontheweb.org/under/waterquality/conductivity.html, 1991.
8. Hoosier RiverWatch, Volunteer Stream Monitoring Training Manual, Fifth Edition, March 2005.